



Contents lists available at ScienceDirect

## Journal of Petroleum Science and Engineering

journal homepage: [www.elsevier.com/locate/petrol](http://www.elsevier.com/locate/petrol)

## Use of a dynamic system and reflectance measurements to assess the impact of monoethylene glycol on calcium carbonate scale

F. Venancio<sup>a</sup>, F.F. Rosário<sup>b</sup>, J. Cajaiba<sup>a,\*</sup><sup>a</sup> Universidade Federal do Rio de Janeiro (UFRJ), Chemistry Institute, Hélio de Almeida St., 40, Cidade Universitária, Rio de Janeiro, 21941-614, Brazil<sup>b</sup> PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello, Cidade Universitária, Rio de Janeiro, State of Rio de Janeiro, 21941-915, Brazil

## ARTICLE INFO

## Keywords:

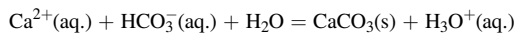
Scale  
Calcium carbonate  
Hydrate inhibitor  
Dynamic test  
Growth rate

## ABSTRACT

The build-up of scale in petroleum production systems is a major hindrance to the efficient production of oil and gas. One of the most common types of scale is calcium carbonate, but the formation of gas hydrate is also a recurring concern, especially in offshore and subsea deep water production. Thermodynamic inhibitors are usually used to avoid hydrate formation, but they contribute to the precipitation of inorganic salts. As monoethylene glycol (MEG) is the most commonly used thermodynamic inhibitor, the purpose of this work was to evaluate the effect of MEG on the formation of calcium carbonate scale using a Dynamic Scale Loop (DSL) to evaluate scale inhibitors. The results show, as expected, that the larger the amount of MEG, the lower the calcium carbonate scale formation time. In addition, to better understand the DSL results and the formation and growth of crystals, focused beam reflectance measurement (FBRM) was performed. The results confirm that the addition of MEG decreases the growth rate by hindering the agglomeration of crystals due to an increase in the viscosity of the solutions.

## 1. Introduction

In oil and gas production, the formation of scale is one of the reasons that wells are shut down (Jamaluddin and Kabir, 2012). Calcium carbonate is one of the most common types of scale (Bezerra et al., 2013; Dyer and Graham, 2002; Kan and Tomson, 2010; Oddo and Tomson, 2000). Therefore, to avoid production downtime, operators invest a portion of their resources in maintenance programs to prevent scale formation, which normally use chemical inhibitors. The general equilibrium involved in calcium carbonate precipitation, in which the pH plays an important role in the process (Gómez-Morales et al., 1996) is defined as:



Another inorganic deposit class that can occur, especially during production in deep water, are hydrates (Khalil De Oliveira and Gonçalves, 2012; Kvenvolden and Lorenson, 2001; Sloan et al., 2009). Gas hydrates are crystalline solids that consist of gas molecules trapped by water molecules (Hight, 1994; Kvenvolden and Lorenson, 2001). Depressurization and a drop in the external temperature (in deep water,

the temperature can reach 4 °C) provide the appropriate thermodynamic conditions for hydrate formation (Rajnauth et al., 2010). Therefore, hydrate inhibitors are commonly used to avoid production downtime.

There are two main classes of hydrate inhibitors: thermodynamic inhibitors, which must be used in large amounts, and the low-dosage inhibitors, that can be classified as kinetic or anti-agglomerant inhibitors. The thermodynamic inhibitors interfere in the chemical equilibrium shift that leads to hydrate formation, while the low-dosage inhibitors act in the crystal growth mechanism (Jordan et al., 2005; Kelland, 2006; Storr et al., 2004).

Monoethylene glycol (MEG), triethylene glycol (TEG), methanol, and ethanol are the most common thermodynamic hydrate inhibitors (Fan et al., 2006). In addition, studies have been conducted to assess potential inhibition with other co-solvents, such as n-propanol (Chapoy et al., 2008). However, these alcohols decrease the solubility of inorganic compounds, due to the increase of Saturation Ratio (SR) of the solution, which is defined as

$$\text{SR}^2 = (a\text{Ca}^{2+} \cdot a\text{CO}_3^{2-}) / K_{\text{sp}}$$

where  $a\text{Ca}^{2+}$  and  $a\text{CO}_3^{2-}$  are the activity of the calcium and carbonate

\* Corresponding author.

E-mail address: [cajaiba@iq.ufrj.br](mailto:cajaiba@iq.ufrj.br) (J. Cajaiba).<https://doi.org/10.1016/j.petrol.2018.02.064>

Received 20 February 2017; Received in revised form 21 February 2018; Accepted 27 February 2018

**Table 1**  
Concentrations used in the dynamic and static tests.

Series	COD	Ca <sup>2+</sup> (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)	MEG content (m/m)
A	A1	4000	4000	0
	A2	4000	4000	21%
	A3	4000	4000	41%
	A4	4000	4000	61%
B	B1	2080	1920	0
	B2	2080	1920	21%
	B3	2080	1920	42%
	B4	2080	1920	61%

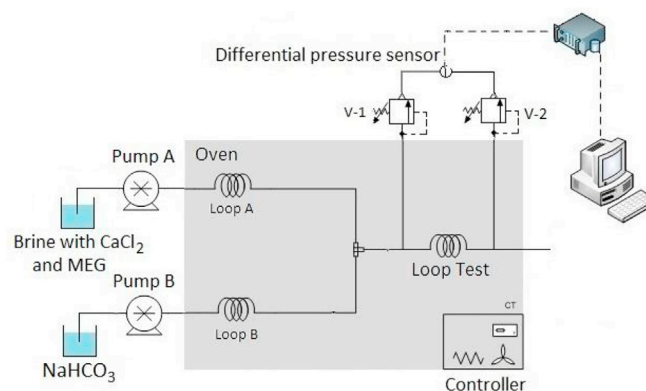
ions, and  $K_{sp}$  is the thermodynamic solubility product. The minimum energy to achieve a stable crystal, known as the critical Gibbs free energy, decreases when the saturation ratio increases (Flaten et al., 2010). As a result, there is a negative consequence for using thermodynamic inhibitors - they contribute to the formation of inorganic precipitates that favor scale formation (Kan et al., 2002; Shipley et al., 2010; Tomson et al., 2005).

However, there is not a large amount of literature regarding the evaluation of inorganic salts with different thermodynamic hydrate inhibitors. Flaten et al. (2010) studied the effect of adding MEG over the time to the crystal formation (induction time) of calcium carbonate using a conductivity cell. They observed an increase in the induction time as the MEG content increased. This result was surprising; since the addition of MEG increases the supersaturation level, a decrease in induction time would be expected. The authors concluded that the viscosity played a key role in this process by hindering the growth of detectable crystalline germs. Tomson et al. (2005) studied the influence of MEG, TEG, and methanol on barium sulfate solubility. They observed decreased solubility with a small amount of the co-solvent and increased solubility when using solutions above 50% v/v concentrations of the alcohols. Sena (2011) analyzed the influence of MEG and ethanol in the calcium carbonate precipitation, verifying that ethanol accelerates the precipitation rate while MEG decreases it. Manoli and Dalas (2000) investigated the influence of ethylene glycol, isopropanol, and ethanol on calcium carbonate precipitation, concluding that the presence of these co-solvents resulted in accelerated growth of these crystals.

Jordan et al. (2005) studied the influence of MEG and methanol on the value of the Minimum Inhibitor Concentration. They used different brines with the potential to precipitate barium sulfate. Unlike their previous work, they carried out the assessment using a dynamic system for evaluations. They found that the addition of MEG and methanol led to the need to increase the dosage of the scale inhibitor.

The use of a dynamic system, known as Dynamic Scale Loop test (DSL), is common in scale inhibitor evaluation of calcium carbonate and others mineral deposits (Bazin et al., 2005; Daniels et al., 2014; Graham et al., 2002; Kelland, 2011; Yuan et al., 1998; Zidovec, 1999; NACE, 2005). However, its use in assessing the effect of the addition of other components on inorganic salts precipitation is less common. To monitor calcium carbonate precipitation and other salts under static conditions, other studies have used Focused Beam Reflectance Measurement (FBRM). This technique is capable of obtaining information based on the number of crystals and gives a particle chord length distribution, which is a function of the true particle diameter distribution. This technique can be used to provide inline data for precipitation, particle count and crystal growth simultaneously (Al Nasser and Al Salhi, 2013; Al Nasser and Al Salhi, 2015; Al Nasser et al., 2008; Sousa and Bertran, 2014; Tadayyon and Rohani, 2000).

The current study has assessed the addition of MEG in calcium carbonate precipitation in high salinity systems using a Dynamic Scale Loop in order to understand the scaling time. In addition, focused beam reflectance measurements were performed to better understand the precipitation and crystal growth process.



**Fig. 1.** Schematic of the dynamic system loop (DSL).

## 2. Material and methods

Calcium chloride dihydrate was used to prepare a stock solution of calcium. Dilutions were then made from the stock solution, followed by the addition of sodium chloride and MEG. Sodium bicarbonate solutions were prepared daily. All solutions were filtered through the Millipore system with a porous glass filter and membrane of 0.45  $\mu\text{m}$ .

The solutions used in the tests for the dynamic and static conditions had concentrations according to the values presented in Table 1:

The pH for all brines with calcium chloride and MEG solutions was adjusted to 6.5 and the salinity to 19,980 mg/L with sodium chloride. Saturation ratio (SR) data was obtained using Multiscala<sup>®</sup> software, and a Brookfield LVDV-II + Pro viscometer was used to measure the viscosity of the solutions.

### 2.1. Experiments under dynamic conditions

Fig. 1 presents a schematic view of the DSL used in the continuous flow experiments.

The equipment operates with two pumps pushing the calcium chloride and sodium bicarbonate solutions. The stainless steel tubes with an inner diameter of 1/8" were assembled in a thermostat-regulated oven maintained at 72 °C. These solutions are mixed inside the loop test and forms calcium carbonate, which deposits on the wall of the tube. The deposits will begin a scale process and will start a pressure difference between the inlet and outlet of the loop test. The increase of the pressure differential depends on the concentration of solutions and co-solvent amount (MEG). The flow rate of injection was 5.000 mL/min for the brine with calcium chloride and MEG solution and 4.600 mL/min for the sodium bicarbonate solution.

### 2.2. Experiments under static conditions

The experiments were performed on an Easymax 102 Mettler Toledo platform. The 100 mL reactor vessel was kept at a 300 rpm stirring rate, and the temperature was maintained at 72 °C during the experiments.

The FBRM equipment (Mettler Toledo Model S400) was inserted into the precipitation vessel to monitor the particle size distributions in the range of 2–1000  $\mu\text{m}$  with a 2-s capture interval. An important drawback of using the FBRM probe is the agglomeration of particles in its sapphire window (Al Nasser et al., 2008). This phenomenon causes an important alteration in the total particle counts. Aiming to avoid this source of error, the FBRM probe was removed from the precipitation vessel every eight minutes to perform its cleaning. The acquisition of data was started two minutes after each cleaning. For every two minutes of data acquisition the average of the time and distribution of particle size parameters was taken. These experiments lasted for ninety minutes.

Download English Version:

<https://daneshyari.com/en/article/8125107>

Download Persian Version:

<https://daneshyari.com/article/8125107>

[Daneshyari.com](https://daneshyari.com)